

# **The Use of Functionalized Nanoparticles as Non-specific Compatibilizers for Polymer Blends**

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## **INTRODUCTION**

Organic-inorganic nano-composites are a very promising class of materials under active investigation. One can in these materials, through nanoscale engineering, combine the flexibility of polymers with the high modulus, flame resistance, and other beneficial properties of the inorganic component and thus produce a new class of lightweight materials. Most prior organic-inorganic nano-composites efforts to improve properties and understand fundamental interactions have focused on the use of organosilicate clays in melts of a single polymer component. Another, more traditional method, for engineering a large variety of materials with carefully controlled properties is blending of various polymers. We have explored the efficacy of combining both techniques in order to overcome some of the fundamental problems inherent in the two technologies when used separately. Our experiments show that high aspect ratio inorganic fillers, with at least one dimension in the nanometer range, can form in-situ grafts by adsorbing large amounts of polymer. These graft composite nano-structures in turn are very effective at reducing the interfacial tension in highly immiscible blends and are thus inducing compatibilization. This phenomenon should be widely applicable to most polymer blends. A variety of model materials primarily based on polystyrene (PS), poly(methyl methacrylate) (PMMA), and polyethylene-propylene (PEP) have been prepared and investigated with the 5.3.2 Polymer STXM and complementary characterization tools.[1] We focus the discussion here on the morphological evolution in PS/PMMA and PS/PMMA/PEP model systems as determined with the 5.3.2 Polymer STXM.

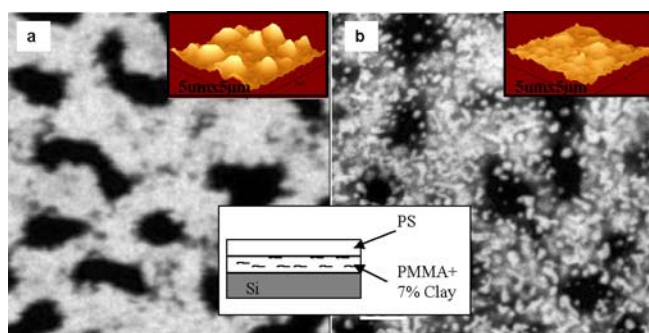
## **EXPERIMENTAL**

100-200nm thick films of the PS/PMMA or PS/PMMA/PEP, with and without fillers, were spun cast onto Si wafers from a common solvent and annealed for up to 96 hours, at  $T=170^{\circ}\text{C}$ , well above the glass transition temperature,  $T_g$ , of all polymers. The samples were quenched to room temperature, i.e. well below the  $T_g$  of PS and PMMA, and transferred to TEM grids for investigation with the 5.3.2 Polymer STXM [2]. Photon energies near the carbon K absorption edge that have selective high cross section for a particular component were used to image the morphology: 285.15 eV for PS, 288.4 eV for PMMA, and 287.6 eV for PEP.

## **RESULTS AND DISCUSSION**

PS/PMMA thin film blends prepared with and without various alkane functionalized montmorillonite clays were investigated. The STXM results (not shown here) clearly showed that the morphologies in the presence of the clay have much smaller domains, often near the

resolution limit of the 5.3.2 Polymer STXM microscope of 40 nm. In contrast, blends without clays have domains many microns in size. Experiments with PS/PMMA bilayers elucidated the mechanism by which the clay is facilitating the compatibilization of the two polymers. Clay was added to the PMMA layer and either preannealed before a PS was placed on top and the film was further annealed, or the PMMA/clay layer was annealed with a PS layer without preannealing. The morphology in the preannealed case is much larger, clearly indicating that if the PMMA is given time to saturate the clay interface, the clay will not be effective as a compatibilizer. In contrast, there seems to be sufficient diffusion if only a single anneal is used to allow co-adsorption of PS and PMMA at the clay interface, thus producing an effective compatibilization agent (See Fig. 1).



**Fig. 1.** STXM PS maps of annealed PS/PMMA bilayer samples. (a) Bottom PMMA layer with 7% clay preannealed at 170° for 24 hrs, (b) bottom layer PMMA with 7% clay w/o preannealing. Both samples were annealed for 72 hrs at 170° after bilayer was formed (Image size 15  $\mu\text{m}$  x 15  $\mu\text{m}$ ). This experiment clearly shows that the formation of PS and PMMA functionalized clay particles that are interfacially active, can only occur if the surfaces of the clay have not already been saturated with PMMA molecules (a). The formation of the active form of functionalized particles is slow enough that the diffusion of PS to the clay particle can occur. - Insets are AFM topographs, showing reduced roughening for the more compatibilized samples.

The effectiveness of the clay was also proven in the even more incompatible PS/PMMA/PEP tertiary polymer system. Figure 2 shows STXM micrographs w/ and w/o clay. Again, the morphology is much smaller in the materials with the clay as a compatibilizing agent.

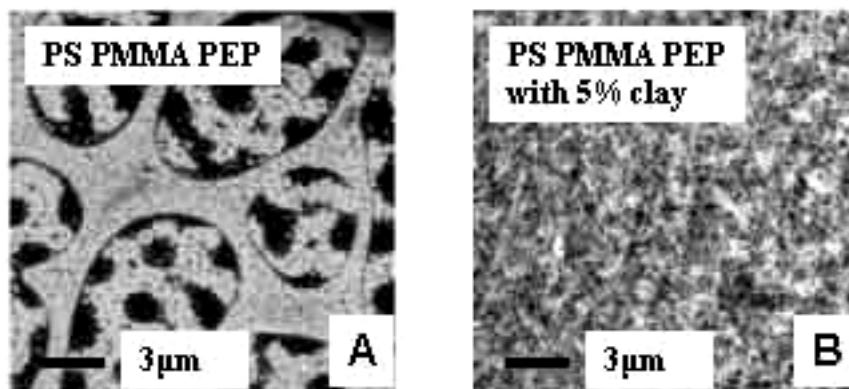


Figure 2. STXM images of PS/PMMA/PEP annealed for 24 hours at 170°C, demonstrating the compatibilization in the presence of clay in even more highly incompatible polymer blend systems.

The imaging properties of the 5.3.2 Polymer STXM were particularly helpful in differentiating the PS, PMMA, and PEP components in the ternary system of those polymers. An example is shown in Figure 3.

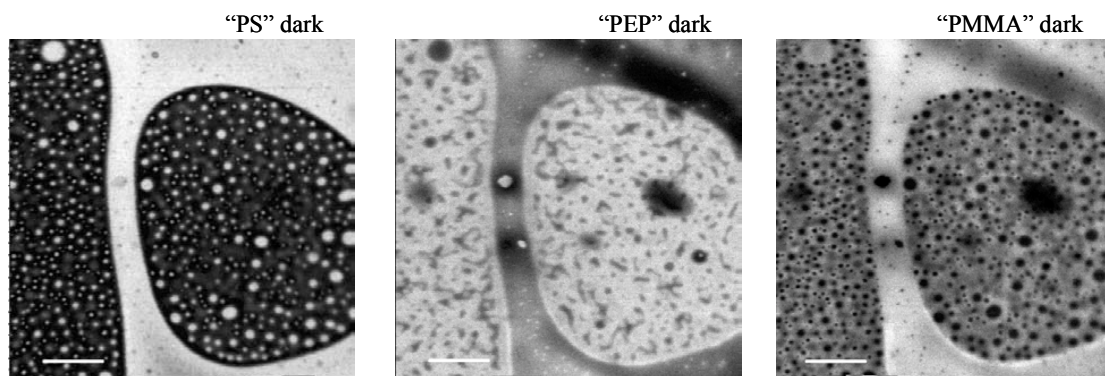


Figure 3. 30x30 micron images of PS/PMMA/PEP tertiary polymer thin film blend without clay imaged at 285.15 eV (PS), 287.6 eV (PEP), and 288.4 eV (PMMA), respectively, to emphasize and delineate the components.

## CONCLUSION

We have shown that alkane-modified montmorillonite clays can be effective compatibilizers of incompatible polymer blends. This opens the door to a new, simple, and cheap process to produce novel inorganic-organic nano-composites.

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## REFERENCES

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2. A. L. D. Kilcoyne, T. Tyliczszak, W.F. Steele, S. Fakra, P. Hitchcock, K. Franck, E. Anderson, B. Harteneck, E.G. Rightor, G.E. Mitchell, A.P. Hitchcock, L. Yang, T. Warwick and H. Ade, *J. Synchrotron Rad.* (in press)

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